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THE USE OF THE FPEECE TECHNIQUE FOR THE INVESTIGATION OF
ELECTROCHEMICAL BEHAVIOR

by

Ulrich Stimming

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2B

The Use of the FREECE Technique
for the Investigation of Electrochemical Behavior

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The background, experimental procedures and some results using the FREECE technique are described. Properties of liquid and frozen $\text{HClO}_4 \cdot 5.5\text{H}_2\text{O}$ with respect to electrical conductivity and deuteron NMR are discussed. Electrochemical behavior of the metal-(liquid or frozen) electrolyte interface as observed in capacity measurements and charge transfer reactions is described. In the case of hydrogen evolution on copper, silver and gold, temperature dependent transfer coefficients are found. For copper and silver, straight Tafel lines with a slope of 85mV independent of temperature result in a transfer coefficient that is proportional to temperature. Some implications of the results for the understanding of electrochemical processes on a molecular level are discussed. The importance of UHV work on water-ion coadsorption on metal surfaces for the understanding of electrochemical processes on a molecular level is emphasized.

In studying interfacial electrochemical behavior, especially in aqueous electrolytes, a variation of the temperature is not a common means of experimentation. When a temperature dependence is investigated, the temperature range is usually limited to 0-80°C. This corresponds to a temperature variation on the absolute temperature scale of less than 30%, a value that compares poorly with other areas of interfacial studies such as surface science where the temperature can easily be changed by several hundred K. This "deficiency" in electrochemical studies is commonly believed to be compensated by the unique ability of electrochemistry to vary the electrode potential and thus, in case of a charge transfer controlled reaction, to vary the energy barrier at the interface. There exist, however, a number of examples where this situation is obviously not so.

There are currently a number of attempts to overcome the limitations of the limited temperature accessible in aqueous electrolytes:

- (i) To use organic solvents that allow one to work at much lower temperatures (1-5);
- (ii) To use an electrolyte with a high boiling point such as concentrated phosphoric acid (6);
- (iii) To work in an aqueous electrolyte under high pressure in order to extend the available temperature range to higher temperatures (7,8);
- (iv) To work in aqueous electrolytes below the freezing point of the electrolyte thus increasing the available temperature range to lower temperatures (9).

The latter approach termed **FREECE** (FRrozen Electrolyte ElectroChEmistry) has been pursued in our laboratory. In addition to increasing the available temperature down to approx. 120K which allows one to vary the temperature by more than a factor of two, there are other interesting aspects of these technique:

- One can study specific low temperature effects, such as possible quantum effects;
- One can study the influence of solidification, i.e. the development of a long range order or a possible glass formation of the electrolyte on electrochemical behavior;
- One is in a better position to compare results in electrochemistry with results in surface science involving water ad- or coadsorption on metal surfaces which are usually investigated in the temperature range 100-250K as done by Sass and co-workers (10,11), Wagner (12) and Madey (13).

In this paper, some of the possibilities associated with the FREECE technique will be described. Results referring to the charge distribution at the electrode-electrolyte interface and to charge transfer reactions will be presented and briefly discussed.

Experimental

Design of Experimental Set-up. In performing electrochemical measurements at cryogenic temperatures, two different approaches can be chosen: Either to adapt an electrochemical cell to a commercially available cryostat or to adapt a cooling system to an optimized electrochemical cell.

While it is convenient to use a standard cryostat, the cell has to be fitted in the sample space of the cryostat and the leads to the cell are usually fairly long - a specific draw-back for impedance measurements. Another disadvantage is the long cool-down times of these systems which may not allow one to rapidly freeze the electrolyte. However, for experiments not requiring sophisticated electrochemical experimentation this may be the most convenient experimental set-up.

Most of the work in our laboratory has been done using specially designed cells that are incorporated in a rather simple cooling device. In working with polycrystalline metal foils, a cell design as pictured in Fig.1 has been used. Metal

foils for working and counter electrode are separated by approx. 1mm, with a reference electrode made of wire close to the gap between the two foils. The reference electrode can be either a hydrogen loaded Pd wire or, in case of a redox electrolyte, a platinum wire or any other metal that establishes the equilibrium potential of the investigated reaction. For the latter situation, overpotentials at all temperatures are directly given by the difference between working and reference electrode. The cell further contains two platinum resistance elements sealed in glass for the temperature control and an independent temperature measurement. The electrolyte volume is approx. 1cm³. A heating wire is wrapped around the cell which is connected to the temperature controller. The cell is placed in an outer jacket which is hooked up to a vacuum regulation system and, in its lower part, is connected with a liquid nitrogen reservoir. By regulating the vacuum, a variable stream of evaporating nitrogen passes the cell and cools it. The temperature controller adjusts a constant temperature by switching the heat on and off. The accuracy of the temperature regulation is about $\pm 1\text{K}$ and the cell has been operated down to 100K. Cells made either of glass or of Kel-F have been used.

In order to investigate specific crystal faces, a cell design has been chosen that is based on the idea of the hanging drop technique often used in single crystal studies. A schematic picture is shown in Fig.2. The central part is a glass block that extends into the lower part where cooling is provided by evaporating liquid nitrogen, while heating wires connected to the temperature controller and wrapped around the glass block establish a constant temperature in a comparable way as described above. On top of the glass block, a gold disk which forms the counter electrode sits in a depression. A drop of electrolyte of 50-100 mm³ can be supplied onto the Au disk. A crystal rod with the desired crystal face pointed down can be lowered by means of a micrometer to contact the electrolyte. A Pd/H wire as reference electrode can also be positioned with a micrometer. The use of micrometers allows for an optimization of the geometry which is crucial at lower temperatures to keep the cell as low-ohmic as possible. A glass sealed thermocouple measures the actual temperature of the electrolyte. Because of the higher thermal mass of this cell, special insulation is necessary in order to reach temperatures below 170K.

Electrochemical Instrumentation. For all electrochemical experiments, regular instrumentation common in electrochemical research can be used. One has to consider, however, that the electrical characteristics of the cell change by many orders of magnitude by changing the temperature from room temperature to cryogenic conditions. The electrolyte that has been widely used in our laboratory is aqueous perchloric acid of the composition $\text{HClO}_4 \cdot 5.5\text{H}_2\text{O}$ which exhibits a relatively high conductivity even at low temperatures. More details regarding this electrolyte will be given below.

For capacity measurements, several techniques are applicable. Impedance spectroscopy, lock-in technique or pulse measurements can be used, and the advantages and disadvantages of the various techniques are the same as for room temperature measurements. An important factor is the temperature dependent time constant of the system which shifts e.g. the capacitive branch in an impedance-frequency diagram with decreasing temperature to lower frequencies. Comparable changes with temperature are also observed in the potential transients due to galvanostatic pulses.

For the investigation of charge transfer processes, one has the whole arsenal of techniques commonly used at one's disposal. As long as transport limitations do not play a role, cyclic voltammetry or potentiodynamic sweeps can be used. Otherwise, impedance techniques or pulse measurements can be employed. For a mass transport limitation of the reacting species from the electrolyte, the diffusion is usually not uniform and does not follow the common assumptions made in the analysis of current or potential transients. Experimental results referring to charge distribution and charge transfer reactions at the electrode-electrolyte interface will be discussed later.

Charge distribution

The charge distribution at metal electrode-electrolyte interfaces for liquid and frozen electrolytes has been investigated through capacity measurements using the lock-in technique and impedance spectroscopy. Before we discuss some of the important results, let us briefly consider some properties of the electrolyte in its liquid and frozen state.

$\text{HClO}_4 \cdot 5.5\text{H}_2\text{O}$ is an aqueous perchloric acid of stoichiometric composition that represents the highest hydrate of the perchloric acid. It crystallizes in a clathrate type of structure at 228K. The crystallographic parameters have recently been determined using X-ray diffraction (14,15). In clathrates one usually has a host lattice with different types of voids. In case of $\text{HClO}_4 \cdot 5.5\text{H}_2\text{O}$ the host lattice is formed by H_2O with ClO_4^- and H^+ as guests. Conductivity measurements indicate a high conductivity in the liquid state, but upon freezing at 228K no abrupt, just a steady, decrease is observed with decreasing temperature; the mobile species are presumably the protons. In order to gain more insight into the conduction process, NMR studies were performed. The measurements were carried out in deuterated perchloric acid solutions since there are some advantages of deuteron versus proton NMR. Below the freezing point, a line broadening increasing with decreasing temperature can be observed. The line broadening can be related to the frequency of the diffusion-reorientation of the deuterons. Fig.3 shows an Arrhenius plot of the conductivity, plotted as the inverse resistance, and of the inverse halfwidth of the line broadening (Huang, T.-H.; Ang, T.T.; Frese, U.; Stimming, U. submitted for publication). It is interesting to note that below 228K, the freezing point of the electrolyte,

the slopes for the line broadening and the conductivity are very similar, corresponding to an activation energy of approx. 0.3eV. At 170K, another break in the slope is observed. This temperature has been identified as a reversible higher order phase transformation (14,15). While the activation energy of the conductivity increases to approx. 0.38eV, the decrease in frequency in the NMR signal is much steeper with approx. 0.7eV. It has to be mentioned, however, that the shape of the NMR signal at very low temperatures suggests that the deuterons are still mobile with a frequency of about 10^3 Hz.

Capacity data has been obtained for gold, silver and copper. As mentioned above, the main effect of temperature on the impedance is a shift of the spectrum to lower frequencies with decreasing temperatures. This is illustrated in Fig.4 for a polycrystalline gold electrode in $\text{HClO}_4 \cdot 5.5\text{H}_2\text{O}$ (Tellefsen, K.; Stimming, U. unpublished results). Comparing the two impedance spectra, the one measured at 278K in the liquid electrolyte and the other measured at 198K in the frozen electrolyte, the effect of temperature is clearly seen. The shape of the spectra is essentially not changed which indicates that the equivalent circuit underlying this interfacial behavior is preserved in the frozen electrolyte. This behavior is also reflected in the potential dependence of the capacity of polycrystalline gold (16). The characteristic peaks in capacity-potential curves observed in the liquid electrolyte are preserved in the frozen electrolyte. The curves in Fig.5 show a structure that is similar to what is observed at room temperature in the liquid electrolyte. With decreasing temperature, these features become less pronounced, and at temperatures below 150K, the curves become rather flat. Similar results were also obtained by Iwasita et al. (17) for polycrystalline gold and by Hamelin et al. (18) for gold (210).

In a similar way, capacity measurements for polycrystalline silver and copper indicate that "electrochemistry" stays intact below the freezing point of the electrolyte. When the minima of capacity-potential curves are plotted as a function of temperature, as shown in Fig.6, a straight line is obtained in the temperature range 200-300K (19). The freezing of the electrolyte does not seem to have any major effect on the electrode capacity of silver and copper. As can be seen from Fig.6, the capacity exhibits a positive temperature coefficient, dC/dT ; this is also observed for gold. This is in contrast to the early results of Grahame on mercury (20) and also on gold by Schmid and Hackerman (21). Hamelin et al. (22), however, observed for Au (210) a positive temperature coefficient at potentials positive of the pzc and a negative temperature coefficient at potentials negative of the pzc in the temperature range 274 to 323K for dilute HClO_4 . It would be interesting to see if e.g. the Grahame results, where the capacity increases with decreasing temperature, are also reflected in capacity behavior of mercury in the frozen electrolyte. Overall, the capacity behavior as found for gold, silver and copper suggests the possibility to use the FREECE technique to study electrochemical behavior in a wide range of

temperatures by passing the freezing point of the electrolyte.

It is tempting to consider, on the basis of these capacity measurements, the consequences for an understanding of the electrochemical double layer. Although it is much too early, with respect to the available data, to justify a qualified attempt, a few aspects seem to be clear enough to allow for some qualitative remarks. The results indicate that the double layer is still intact in the frozen electrolyte. The solidification of the electrolyte with its development of a long range order obviously affects the interfacial region only in a minor way. One reason certainly is that the electrolyte is highly concentrated; $\text{HClO}_4 \cdot 5.5\text{H}_2\text{O}$ corresponds to an approx. 7M HClO_4 in water. This limits the potential drop to the very interface, excluding diffuse layer effects, i.e. there is no extension of the potential drop into the bulk of the electrolyte. The charging of the interface as a function of the electrode potential can still be achieved since, as found from the NMR measurements, the protons are mobile in the frozen electrolyte. Reversing the point of view, one can then ask why is the capacity behavior in the liquid electrolyte so similar to that in the frozen electrolyte. In the frozen state, the electrolyte will, ideally, terminate at the electrode in some kind of structured way, at least in the two dimensions parallel to the metal surface. Normal to the surface some differences may exist, especially at the locations of charge and counter-charge where a high electric field exists. The locations of charge depends on the proton mobility not only normal but also parallel to the surface. Any anisotropy effects of the proton mobility are not known for $\text{HClO}_4 \cdot 5.5\text{H}_2\text{O}$ and the crystal structure does not suggest any (14,15). This arrangement can stay essentially preserved upon melting, especially close to the surface where the field may stabilize advantageous orientations of the water with the perchlorate ions and the protons. In addition, it is well known that aqueous solutions and pure water form large agglomerates in the liquid state that allow e.g. X-ray diffraction to be observed. In summary, regarding the molecular processes at the electrode-electrolyte interface, they do not seem to be strongly affected by the phase change from liquid to solid of the bulk electrolyte.

Charge transfer reactions

Charge transfer reactions represent an important category of electrochemical behavior. As already pointed out above, an appropriate investigation of kinetic parameters of electrochemical reactions in aqueous electrolytes suffers from the small temperature range experimentally accessible. In the following, some preliminary results using the FREECE technique are presented for the $\text{Fe}^{2+}/\text{Fe}^{3+}$ redox reaction and for hydrogen evolution at various metal electrodes.

The redox reaction $\text{Fe}^{2+}/\text{Fe}^{3+}$ was the first reaction for which it could be demonstrated that the investigation of electrochemical behavior in frozen aqueous electrolytes is possible (9). The electrolyte was 1M HClO_4 which has the

disadvantage that below 273K one has a temperature dependent composition of the liquid electrolyte in addition to ice and eventually a solid mixture of ice and the eutectic of ice and $\text{HClO}_4 \cdot 5.5\text{H}_2\text{O}$. This rather complicated situation led to the choice of $\text{HClO}_4 \cdot 5.5\text{H}_2\text{O}$ as electrolyte which has a defined freezing point at 228K and is always a single phase except at the freezing point itself.

The exchange current density of the $\text{Fe}^{2+}/\text{Fe}^{3+}$ reaction in $\text{HClO}_4 \cdot 5.5\text{H}_2\text{O}$ has been investigated using galvanostatic pulses in the potential regime of the linear current-potential relationship. Current pulses have to be chosen such that a steady state potential is reached. This procedure allows for an easy separation and also determination of the ohmic drop and the charge transfer overpotential. Results were obtained for various concentrations and are plotted in an Arrhenius plot in Fig.7 (Dinan, T.; Stimming, U. unpublished results). As expected, straight lines are found in the liquid electrolyte with a slope that corresponds to an activation energy of 0.3eV, the common value for this reaction. The concentration dependence also represents, as expected, a reaction order of one. Upon freezing, an increase of the exchange current is observed and the temperature has to be several ten degrees below the freezing point in order for the current to come back to the same value as at the freezing point. The current for the two highest concentrations, 0.03M and 0.01M, becomes almost identical upon freezing. At lower temperatures, the differences between the values for 0.01M and 0.003M also seem to diminish to eventually become of comparable value. The difference between the curves for 0.001M and 0.003M, however, stays constant and is approx. a factor of three, as expected for a reaction order of one. The reason for the non-proportionality of the current at higher concentrations is probably due to a limited solubility of the redox system in the electrolyte. Precipitation, or better, crystallization, as opposed to a solid solution of the redox system in the electrolyte, may lead to a reduction of the effectively available number of Fe^{2+} and Fe^{3+} sites at the interface. If the concentration is low enough, the distribution is obviously as random as one would expect it to be similarly to the liquid. From the slope of the curves for lower concentrations an activation energy of 0.35eV can be calculated slightly higher than the value in the liquid electrolyte. This, together with the current increase at the freezing point, results in a considerably higher pre-exponential factor. It will be shown later that the current increase upon freezing of the electrolyte seems to be a rather typical phenomenon and is also observed for the hydrogen evolution reaction at various metal electrodes. Recently, Matsunaga et al. (23) have investigated the $\text{Fe}^{2+}/\text{Fe}^{3+}$ reaction in 1M HClO_4 and in $\text{HClO}_4 \cdot 5.5\text{H}_2\text{O}$ in the liquid and frozen state of the electrolyte. While their results in 1M HClO_4 are very similar to our earlier results (9), the Arrhenius plot for $\text{HClO}_4 \cdot 5.5\text{H}_2\text{O}$ as electrolyte differs considerably from the results shown in Fig.7. In particular, Matsunaga et al. observe a drop in the exchange current density by more than three

orders of magnitude between 180 and 175K. It is currently not clear what the reasons for these differences are.

Hydrogen evolution, the other reaction studied, is a classical reaction for electrochemical kinetic studies. It was this reaction that led Tafel (24) to formulate his semi-logarithmic relation between potential and current which is named for him and that later resulted in the derivation of the equation that today is called "Butler-Volmer-equation" (25,26). The influence of the electrode potential is considered to modify the activation barrier for the charge transfer step of the reaction at the interface. This results in an exponential dependence of the reaction rate on the electrode potential, the extent of which is given by the transfer coefficient, α .

The first system studied using FREECE was the hydrogen evolution on platinum (27). The reaction proceeds similarly in liquid and frozen $\text{HClO}_4 \cdot 5.5\text{H}_2\text{O}$. It exhibits a potential dependence of the current with $\alpha=2$ which is practically the same in the liquid and the frozen electrolyte. The potential dependence indicates, however, that not the charge transfer step but the recombination of hydrogen atoms and/or the diffusion of molecular hydrogen from the surface is rate determining (28).

In contrast to platinum, the hydrogen evolution on copper, on silver and on gold show a different behavior. Similarly to platinum, slow potentiodynamic sweeps have been used to measure the current-potential curves (29). While the behavior of gold shows potential and temperature dependent changes of the slope, silver and copper exhibit straight lines in a Tafel plot, however, with no or only little change of the slope with temperature. This is illustrated in Fig.8 for silver in the temperature range of 140-300K. As can be seen from Fig.8, the lines are straight over about three order of magnitude and almost ideally parallel in the range $T=160-300\text{K}$ with a Tafel slope of $b=85\text{mV}$. The results for copper are very similar. Calculating the transfer coefficient according to $b=RT/\alpha nF$ consequently results in a temperature dependent transfer coefficient as shown in Fig.9 for silver and copper (ref.19). In the temperature range from 160 to 300K a linear dependence of α vs. T is found with a negligible intercept at $T=0\text{K}$.

This result is quite in contrast to the common expectation that the electrode potential changes the activation barrier at the interface which would result in a temperature independent transfer coefficient α . Following Agar's discussion (30), such a behavior indicates a potential dependence of the entropy of activation rather than the enthalpy of activation. Such "anomalous" behavior in which the transfer coefficient depends on the temperature seems to be rather common as recently reviewed by Conway (31).

Analyzing the data in terms of the Arrhenius equation leads to a complementary result (ref.19). An Arrhenius plot of the data obtained on copper is shown in Fig.10. Straight lines are obtained for different potentials in the liquid and in the frozen electrolyte, again with an increase of the current at the freezing point. The lines are nearly parallel for the

various potentials. This results in almost potential independent activation energies between 0.4 and 0.5eV (Fig.11a). The pre-exponential factor, on the other hand, as obtained from the extrapolation to $1/T=0$, is strongly potential dependent (Fig.11b). It is higher in the frozen electrolyte and changes by approx. five orders of magnitude over a range of just 300mV in overpotential!

The latter discussion confirms the results of the potential dependence of the current in that the activation barrier for the hydrogen evolution reaction is, at least on copper and silver, not affected by the electrode potential. This behavior is, on the other hand, connected with the observation of straight lines in a Tafel plot. It would be premature to come up with a comprehensive model that would explain this behavior; more experimental work is necessary to substantiate and quantify the effects for a larger variety of systems and reactions. A few aspects, however, should be pointed out.

(i) It is difficult to conceive that impurity adsorption or the like could account for such radical effects, i.e. that the potential dependence of the activation energy is completely shifted to a potential dependence of the pre-exponential factor.

(ii) A potential dependent coverage with hydrogen may account for some of the observed effects. However, surface science studies indicate that hydrogen is not adsorbed on silver or copper (10), but electrochemical systems may be different since the change of the electrode potential, i.e. the Fermi level, may alter this situation.

(iii) Tunneling effects may play a role which would express themselves in the pre-exponential factor; it is not clear, however, if the tunneling probability would exhibit such a strong potential and temperature dependence.

For an understanding of these processes more information from in-situ surface science experiments is desirable. The study of water adsorption on silver is a good example for providing molecular information that may be relevant for the understanding of electrochemistry. As reviewed by Thiel and Madey (13), water, even in amounts of fractions of a monolayer, does not specifically interact with the silver surface. No differences are found in the thermodesorption spectra are found from submonolayer to multilayer coverages: they all show a single desorption peak typical of bulk ice. The bond structure within the phases is obviously much stronger than between the phases, i.e. in the interfacial region. The orientation of the water molecules is thus determined by the water phase rather than by the influence of the substrate.

Applying this to our electrochemical system could qualitatively explain some of the observed effects. Assuming that there is only a weak interaction between metal and the perchloric acid hydrate, protons being part of the clathrate structure may not be in a favorable position for a charge transfer reaction at the interface. This could result in small pre-exponential factors. The electrode potential, however, may

have a large influence on it since the protons are also the charge carrier that allow the potential difference to be established at the interface. Thus by charging the interface, the protons with the water structure surrounding them, will also be changed which, in turn, influences the hydrogen evolution reaction. Such an effect would be expressed in a potential dependent pre-exponential factor.

Conclusions

It is possible to investigate electrochemical behavior in aqueous electrolytes in a wide range of temperatures by using the FREECE technique. This way, using $\text{HClO}_4 \cdot 5.5\text{H}_2\text{O}$ as electrolyte, temperatures down to approximately -140°C can be reached. The results show that double charging and faradaic reactions occur in the frozen electrolyte in a comparable way as is known for the liquid electrolyte. The electrode capacities for gold, silver and copper decrease with decreasing temperature. The results for the hydrogen evolution on these metals indicate an anomalous behavior in that the transfer coefficient shows a temperature dependence. In the case of copper and silver the transfer coefficient appears to be proportional with temperature. It seems that current models have little ability to explain this behavior. It is expected that microscopic models of the electrochemical interface are better suited. In this respect, the concept of studying the co-adsorption of water and ions on defined surfaces under u.h.v. conditions developed by Sass et al. (10,11) and recently also applied by Wagner et al. (12) can be very helpful for a better understanding of these questions.

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Literature Cited

- (1) VanDyne, R.P.; Reilley, C.N.
Anal.Chem. 1972 44 142.
- (1) VanDyne, R.P.; Reilley, C.N.
Anal.Chem. 1972 44 153.
- (3) VanDyne, R.P.; Reilley, C.N.
Anal.Chem. 1972 44 158.
- (4) Conway, B.E.; Salomon, M. J.Chem.Phys. 1964 41 3169.
- (5) Conway, B.E.; McKinnon, D.J.; Tilak, B.V.
Trans.Faraday Soc. 1970 66 1203.
- (6) Yeager, E.; Scherson, D.; Simic-Glavaski, B.
163rd Meeting of the Electrochemical Society,
San Francisco, 1983, Ext.Abstract #706.

- (7) McDonald, A.C.; Fan, F.F.; Bard, A.J. J.Phys.Chem. 1986 90 196.
- (8) Flarsheim, W.M.; Tsou, Y.; Trachtenberg, I.; Johnston, K.P.; Bard, A.J. J.Phys.Chem. 1986 90 3857.
- (9) Stimming, U.; Schmickler, W. J.Electroanal.Chem. 1983 150 125.
- (10) Sass, J.K. Vacuum 1983 (1983) 741.
- (11) Stuve, E.M.; Bange, K.; Sass, J.K. In Trends in Interfacial Electrochemistry; Silva, A.F., Ed.; D.Reidel Publishing Company: Dordrecht, 1986; p.255.
- (12) Wagner, F.T.; Moylan, T.E. Surf.Sci. 1987 182 125.
- (13) Thiel, P.A.; Madey, T.E. Surf.Sci.Rep. 1987 7 211; and references of T.E.Madey's work therein.
- (14) Wiebke, M.; Mootz, D. Z.Kristallogr. 1985 170 194.
- (15) Mootz, D.; Oellers, E.-F.; Wiebke, M. J.Am.Chem.Soc. 1987 109 1200.
- (16) Dinan, T.; Stimming, U. J.Electrochem.Soc. 1986 133 2662.
- (17) Iwasita, T.; Roettgermann, S.; Schmickler, W. J.Electroanal.Chem. 1985 196 203.
- (18) Hamelin, A.; Roettgermann, S.; Schmickler, W. J.Electroanal.Chem. 1987 230 281.
- (19) Frese, U.; Stimming, U. In Principles of Electrochemical Processes; Schultze, J.W., Ed.; VCH-Verlagsgesellschaft: Weinheim, 1986; DECHEMA Monographs Vol. 102, p.247.
- (20) Grahame, D.C. J.Am.Chem.Soc. 1957 79 2093.
- (21) Schmid, G.M.; Hackerman, N. J.Electrochem.Soc. 1963 110 440.
- (22) Hamelin, A.; Stoicoviciu, L.; Silva, F. J.Electroanal.Chem. 1987 229 107.
- (23) Matsunaga, A.; Itoh, K.; Fujishima, A.; Honda, K. J.Electroanal.Chem. 1986 205 343.
- (24) Tafel, J. Z.Phys.Chem. 1905 50 641.
- (25) Butler, J.A.V. Trans.Faraday Soc. 1924 19 729.
- (26) Erdey-Gruz, T.; Volmer, M. Z.Phys.Chem. 1930 150 203.
- (27) Frese, U.; Iwasita, T.; Schmickler, W.; Stimming, U. J.Phys.Chem. 1985 89 1059.
- (28) Ludwig, F.; Sen, R.K.; Yeager, E. Elektrokhimiya 1977 13 847.
- (29) Frese, U.; Stimming, U. J.Electroanal.Chem. 1986 198 409.
- (30) Agar, J.N. Disc.Faraday Soc. 1947 11 81.
- (31) Conway, B.E. In Modern Electrochemistry; Bockris, J.O'M., Conway, B.E. and Yeager, E., Eds.; Plenum Press: New York, 1987; Vol.16.

Figure 1. Electrochemical cell for cryogenic measurements.

Figure 2. Electrochemical cell for measurements with single crystals at cryogenic measurements.

Figure 3. Arrhenius plot of electrical conductivity of $\text{HClO}_4 \cdot 5.5\text{H}_2\text{O}$ and of the halfwidth of the $^2\text{H-NMR}$ signal.

Figure 4. Impedance spectrum of gold in liquid (278K) and frozen (198K) $\text{HClO}_4 \cdot 5.5\text{H}_2\text{O}$.

Figure 5. Capacity-potential curves of gold at various temperatures in the frozen electrolyte (taken from ref.16, with permission of the Electrochemical Society, Pennington, NJ).

Figure 6. Temperature dependence of the electrode capacity of copper and silver (taken from ref.(16), with permission of the Electrochemical Society, Pennington, NJ).

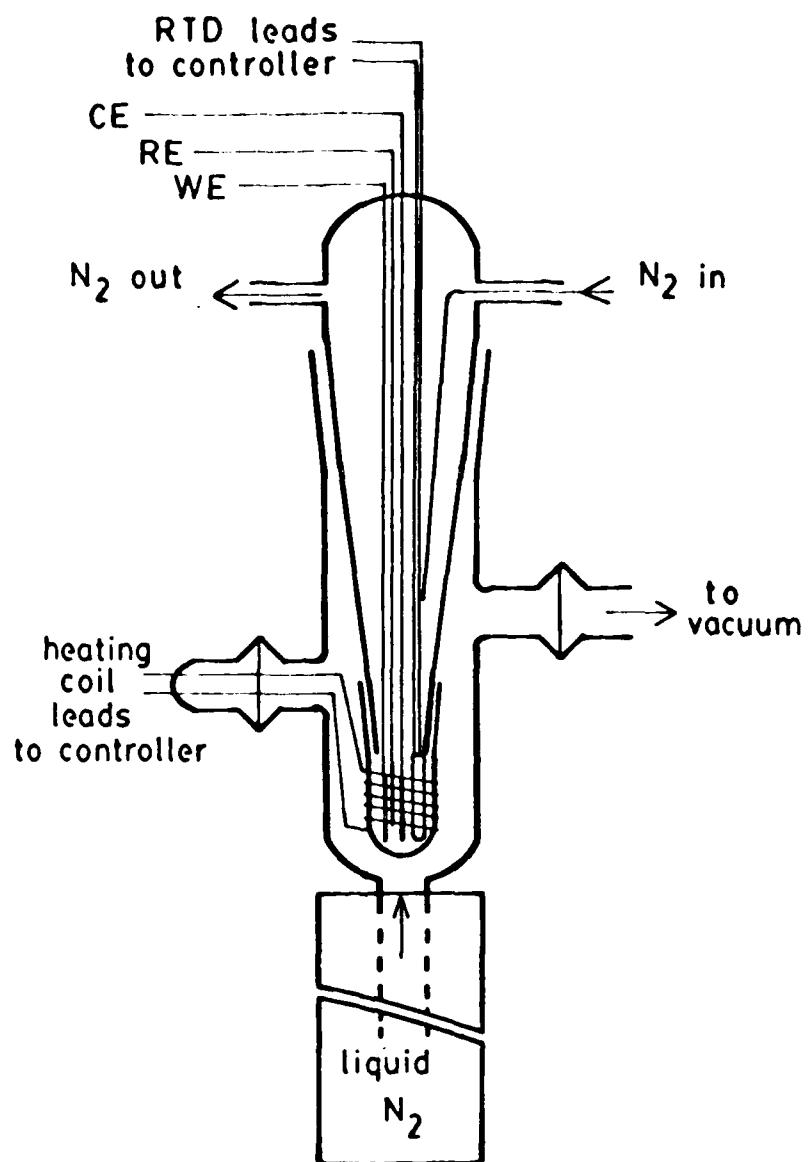
Figure 7. Arrhenius plot of the exchange current density of the $\text{Fe}^{2+}/\text{Fe}^{3+}$ reaction for various concentrations.

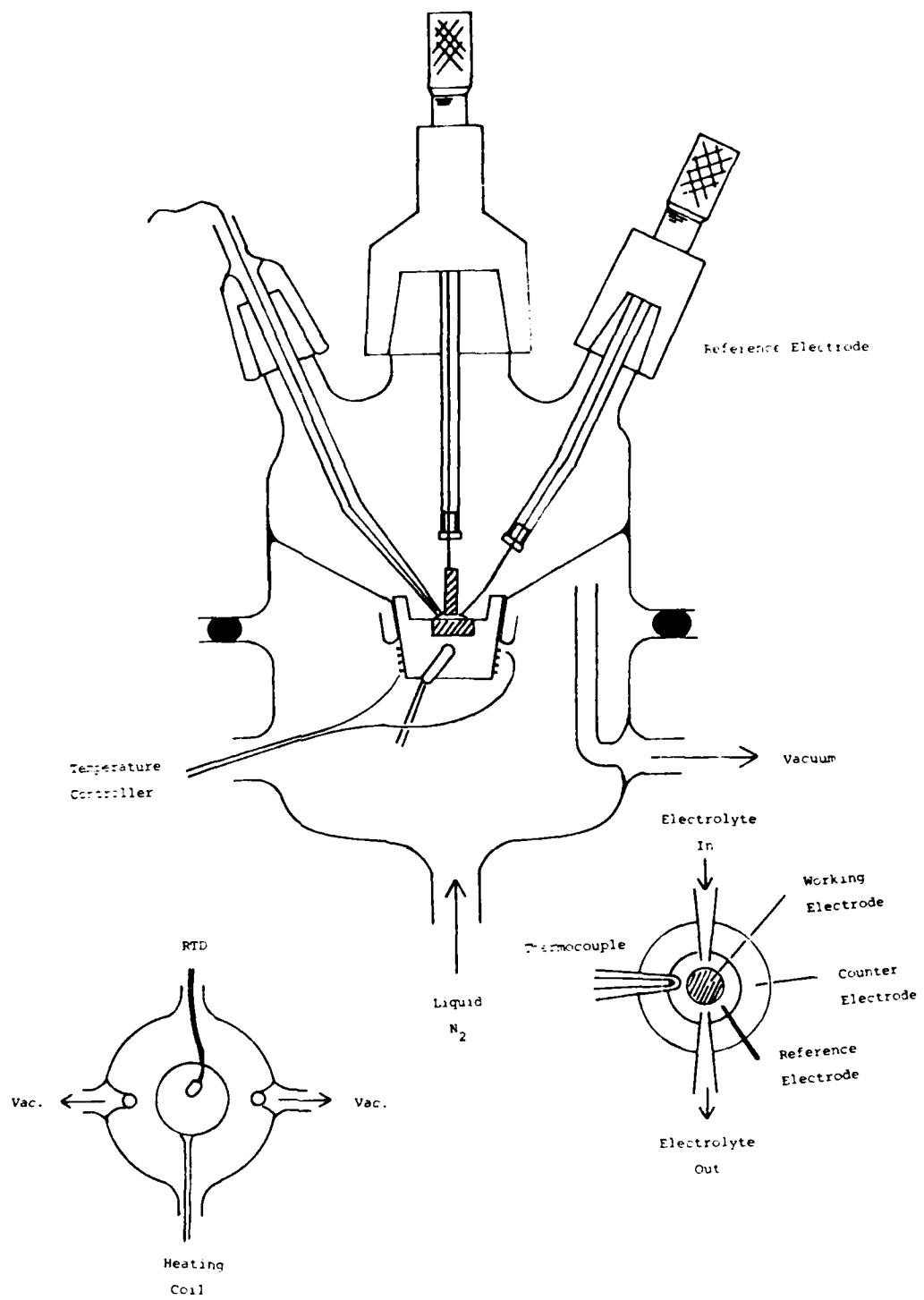
Figure 8. Tafel plot of the hydrogen evolution on silver at various temperatures.

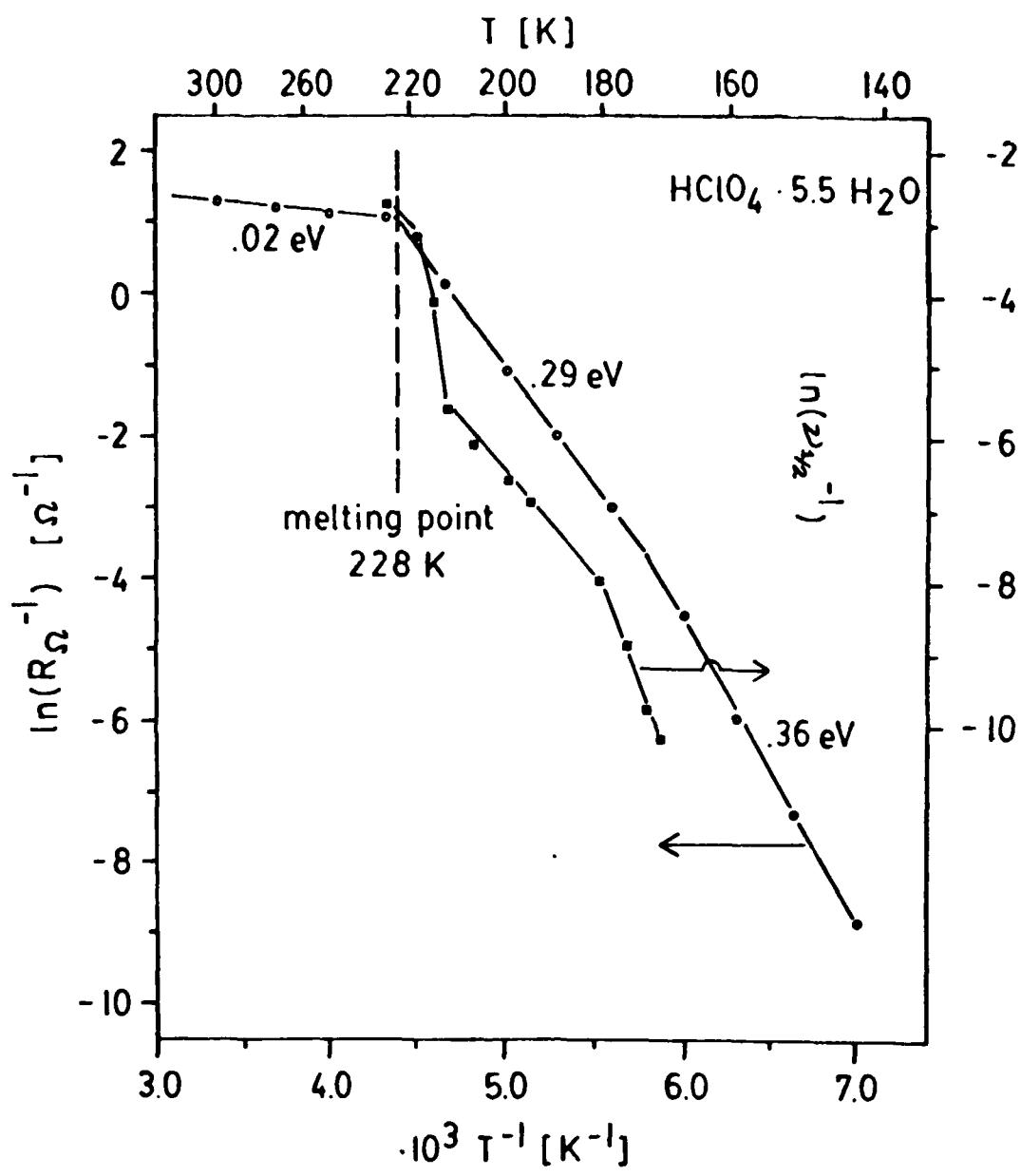
Figure 9. Temperature dependence of the transfer coefficient of the hydrogen evolution on silver and copper.

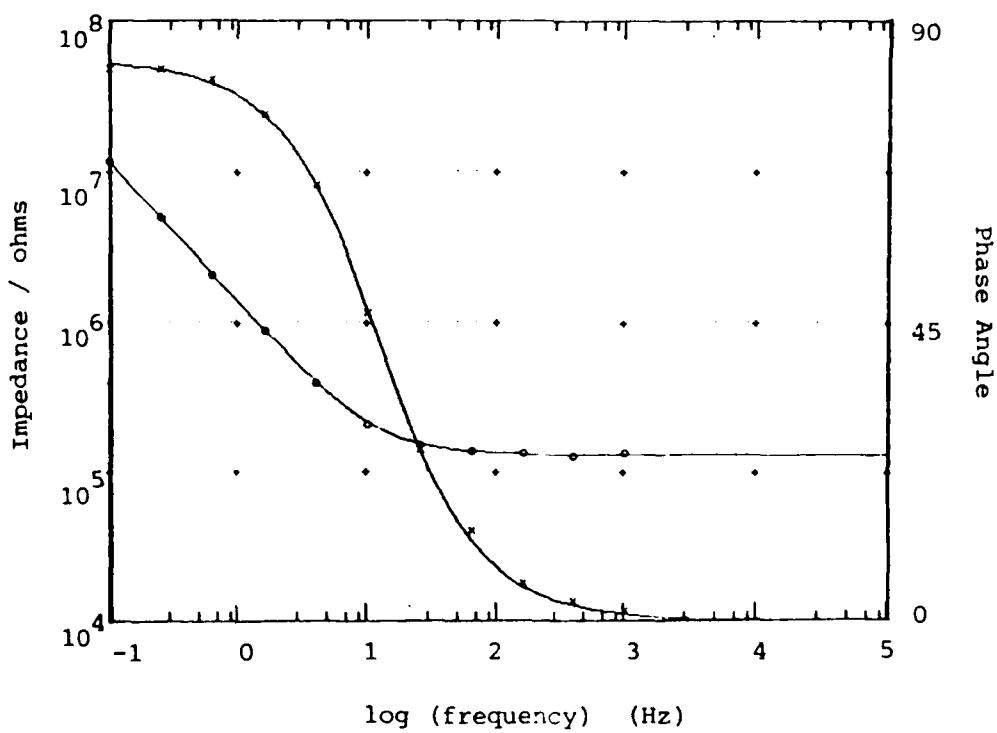
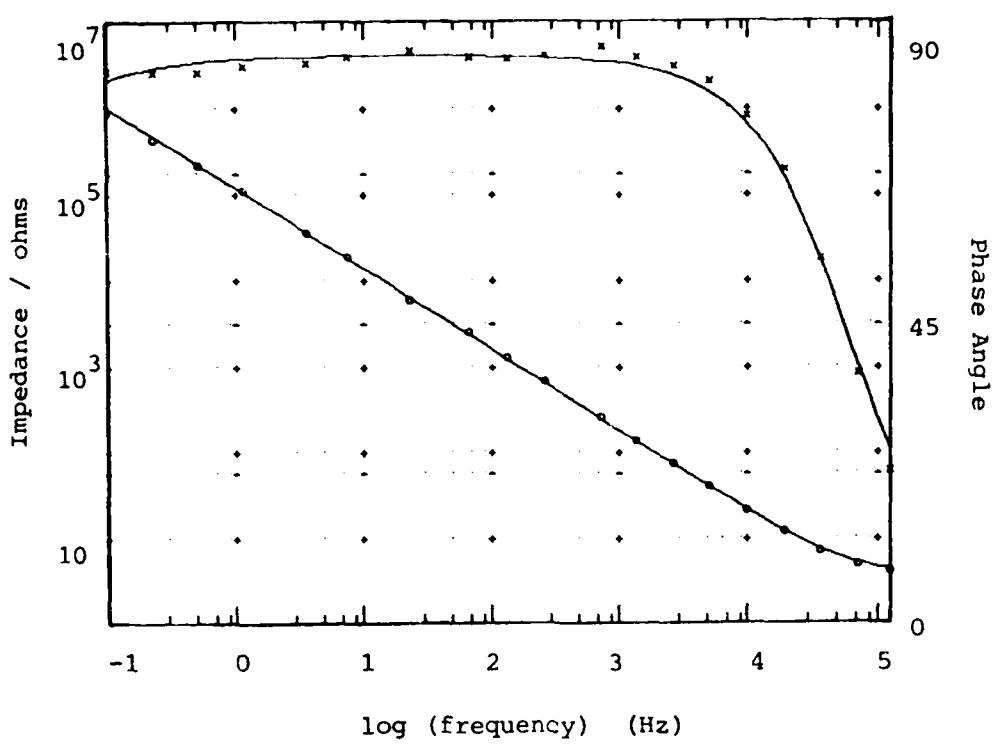
Figure 10. Arrhenius plot of the hydrogen evolution on copper at various potentials.

Figure 11. Potential dependence of the activation energy, E_a , (a) and pre-exponential factor, A , (b) as obtained from Fig.10.









$\text{Au} / \text{HClO}_4 \cdot 5.5 \text{H}_2\text{O}$

